



Project report – Grant FA23860814096, "Fire resistance of geopolymer concretes" – J. Provis, University of Melbourne

1. Background and experimental program

This project provided funding for us to carry out fire testing of geopolymer concrete specimens and associated laboratory testing. The focus of this report will be the outcomes of the series of pilot-scale (4'×4'×6") tests on geopolymer concrete panels, which were conducted on a single geopolymer concrete formulation ("E-Crete 40", supplied by Zeobond Pty Ltd. E-Crete is a trademark of Zeobond). Geopolymer concrete is derived from coal fly ash and metallurgical slag, which are reacted together with an alkaline "activating solution" (sodium silicate in this case), blended with fine and coarse aggregate (quartz sand and crushed granite in this case) to generate a product which is similar in mechanical properties and general appearance to Portland cement concrete.

Geopolymer concrete has been proposed as an alternative to Portland cement concrete in applications requiring high degrees of fire resistance, because the intrinsic chemistry of the geopolymer binder does not require the retention of water of hydration within gel phases to maintain structural integrity of the binder. Portland cement concrete contains a high level of chemically bound water which is essential to the gel binder structure, and which is lost upon heating to several hundred degrees Celsius, whereas the water present within a geopolymer concrete is overwhelmingly present in pores and is not an essential part of the strength-generating phases. However, predictions of geopolymer concrete fire performance have up to this time generally been based on small-scale laboratory testing (usually on paste or mortar specimens) rather than the study of large concrete sections, which provides significance to this work.

E-Crete™ samples were poured, finished and sealed in plastic sheeting for a specified number of days (1, 3, 7, 14 or 28), and then unwrapped and allowed to continue ageing under ambient conditions (Melbourne, Australia, in autumn; 15-25°C daily temperature variations and moderate humidity) to reach 56 days of age. Testing was then carried out following the Standard Time-Temperature Curve (ISO 834-1/EN 1363-1/ASTM E 119) for a test duration of 4 hours:

$$T(^{\circ}C) = 345 \ln(8t + 1) + 20; \quad t \text{ in minutes}$$

Note that the full ASTM testing procedure includes the application of a water jet after the conclusion of the furnace test for the award of a formal fire rating; however, it was not feasible to conduct this aspect of the Standard test procedure, so any discussion of fire rating times presented in this report must be treated as indicative rather than being claims of obtention of a rating according to the Standards.

Report Documentation Page			Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.				
1. REPORT DATE 21 MAR 2010		2. REPORT TYPE Final		3. DATES COVERED 11-09-2008 to 11-10-2009
4. TITLE AND SUBTITLE Fire resistance of geopolymers concretes			5a. CONTRACT NUMBER FA23860814096	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) John Provis			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Melbourne, University of Melbourne, Victoria, Australia, AU, 3010			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Asian Office of Aerospace Research & Development, (AOARD), Unit 45002, APO, AP, 96338-5002			10. SPONSOR/MONITOR'S ACRONYM(S) AOARD	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-084096	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT This project carried out fire testing of geopolymer concrete specimens and associated laboratory testing. This report focuses on the outcomes of the series of pilot-scale (4????) tests on geopolymer concrete panels, which were conducted on a single geopolymer concrete formulation (?E-Crete 40?, supplied by Zeobond Pty Ltd. E-Crete is a trademark of Zeobond). Geopolymer concrete is derived from coal fly ash and metallurgical slag, which are reacted together with an alkaline ?activating solution? (sodium silicate in this case), blended with fine and coarse aggregate (quartz sand and crushed granite in this case) to generate a product which is similar in mechanical properties and general appearance to Portland cement concrete.				
15. SUBJECT TERMS Ceramics, Composites, Polymer Chemistry				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 7
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified		

2. Temperature profiles

Figure 1 presents the final temperatures observed at different points within the specimens cured for different durations. The maximum unexposed face (i.e. the side furthest from the furnace) temperature observed was 105.3°C, in the 14-day sample. ASTM E 119 specifies a maximum allowable temperature rise of 250°F (139°C); given an ambient temperature range of 25-30°C on the dates of testing, the temperature rise observed in all samples is clearly within the requirements of the Standard for a 4-hour fire rating.

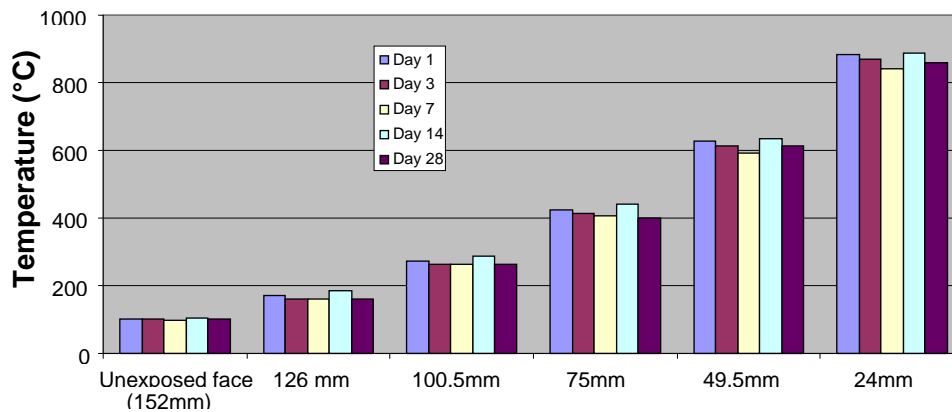


Figure 1. Maximum temperatures recorded at different points in the sample at the end of a 4-hour test (furnace temperature at 4 hours is approximately 1150°C) as a function of distance from the exposed (heated) face. Legend refers to the number of days after pouring that the sample was kept sealed before exposure to ambient conditions.

Figure 2 shows the thermocouple temperature readings as a function of time for one of the samples tested (the 7-day cured sample). A gradual increase of temperature is observed as a function of test duration, with a heating front moving progressively through the sample as the furnace temperature increases (reaching 1000°C after 86.5 minutes). Each data set shown in Figure 2 is the average of the readings from two thermocouples located at each depth, with banks of thermocouples located at different points in the sample, above and below the mid-point.

It is of interest to note that each data set shows an apparent flattening of the rate of temperature increase at a temperature between 100-160°C, holding at this temperature for a period of time, and then an acceleration following this as the temperature starts to increase again. This can be associated with the passage of a boiling front through the material; the concrete initially contains a significant quantity of liquid water in its pores. As this begins to be heated (close to the inside face of the concrete), the water expands upon heating, and fairly soon localized boiling commences. This generates pressure within the pore network of the concrete, forcing the water to flow away from the heated face. This water carries thermal energy as it travels through the sample, causing additional heating of the parts of the sample close to the unexposed face on top of the

heat transport due to conduction through the sample. The full description of the process of heating of concrete requires a fully coupled heat and mass transport model involving flow through the porous concrete structure, microstructural changes in the binder as a function of heating, and consideration of pore pressure effects. Various research groups have published work in this area; we have not yet implemented such a model in detail for geopolymers, although initial modeling work has shown promising outcomes and we certainly plan to continue this line of investigation.

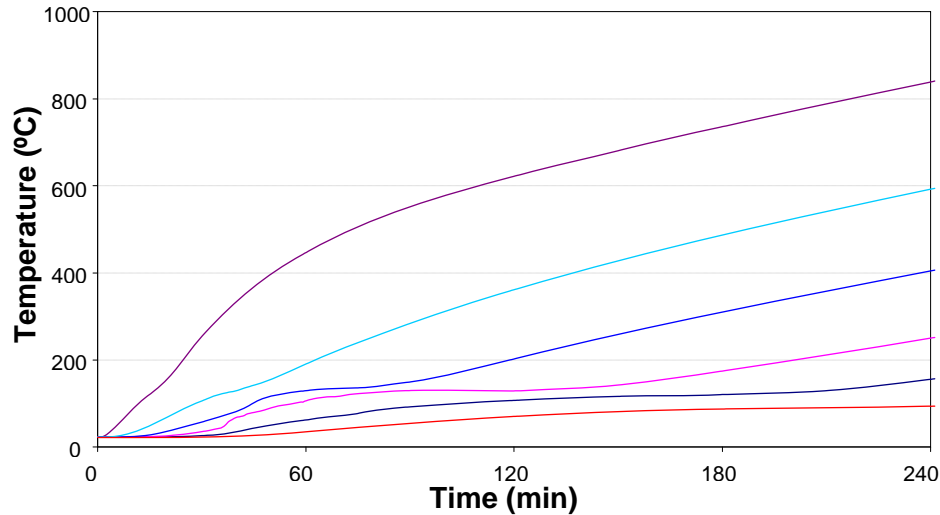


Figure 2. Evolution of temperature profile during the test duration; thermocouple locations are as shown in Figure 1, with temperature decreasing with increasing distance from the exposed face (maroon line at top is 24mm depth, orange line at bottom is the unexposed face).

A small amount of liquid water is observed to flow from the front face of the concrete during the test; the time at which this starts to happen, and the volume of water released, both increase with increasing curing duration, as shown in Figure 3. Figure 3 shows that the water released from the front face of the concrete appears to be ‘channeled’ along the thermocouple banks and cables embedded in the material, and so emerges from these specific places on the faces of the specimens rather than being uniformly distributed. The greater extent of water release from the samples with longer curing duration can be correlated directly with the microstructural evolution of the samples during sealed curing. Sealed curing of the samples enhances water retention, and therefore provides more scope for development of a high degree of reaction and a compact binder microstructure before the water (required to mediate reaction processes) is lost upon drying. There are also believed to be some hydration reactions (i.e. formation of binder phases including chemically bound water) in these mixed fly ash-slag geopolymer systems, and these will also obviously be enhanced by longer periods of sealed curing and the availability of more water. This was observed on an empirical level by the fact that the water released from the better-cured samples appeared to contain more sulfur compounds (which have a

green color and characteristic odor); sulfur is released into the pore solution as slag particles react.

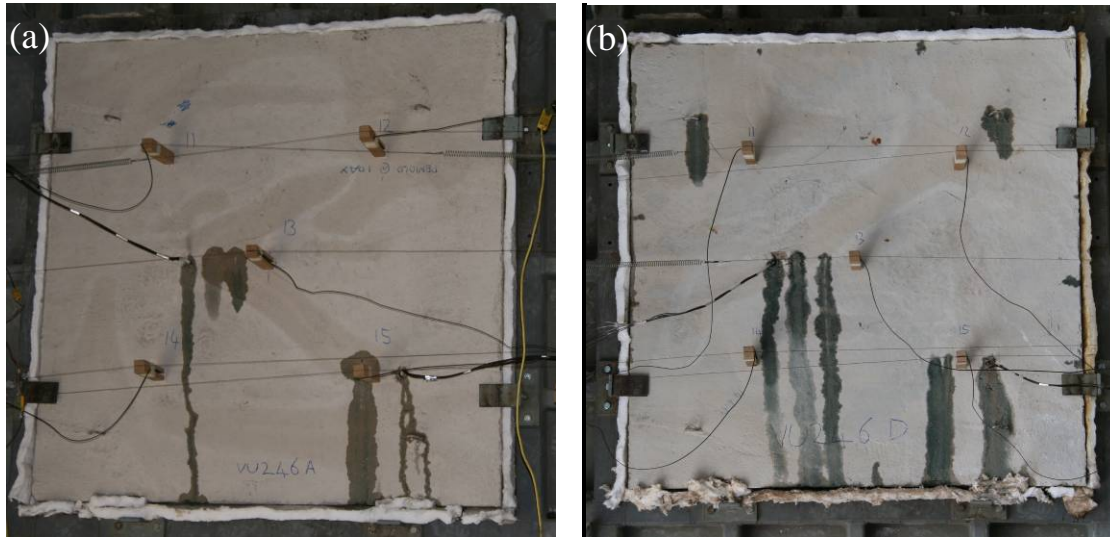


Figure 3. Photographs of the specimens during the test, showing the dependence on curing duration of the volume of water released by the specimens. (a) 1-day cured specimen; (b) 14-day cured specimen. Both photographs taken approximately 60-90 minutes from commencement of the test.

The presence of more water in the samples cured for longer durations provides two competing effects relating to heat transport, which may be used to explain some of the trends displayed in Figure 1. The specific heat capacity and the latent heat of vaporization of water are high, which means that the requirement to heat and then boil more water provides a ‘heat sink’ effect which reduces the rate of temperature increase of the sample. The change in specific heat upon removal of liquid water from the pore structure of the geopolymer can be clearly observed in Figure 1, as there is an obvious change in the gradient of the heating curves before and after the boiling regime. This is most visible in the purple curve (thermocouple bank 24mm from the heated face), as the boiling process is the most rapid at this location; the dry geopolymer above 180°C has a much lower specific heat capacity than the geopolymer with liquid-filled pores below this temperature.

However, the convective heat transfer effects associated with the flow of water through the sample are also significant, with heated water flowing through the pore system of the sample and carrying heat energy with it towards the unexposed face. Additionally, the thermal conductivity of a liquid-filled pore is markedly higher than that of a gas-filled pore, meaning that the overall thermal conductivity of a wetter sample will be higher. The interplay between these effects means that the 1-day cured sample in Figure 1 is heated rather rapidly, as its water content is insufficient to provide a strong heat-sink effect (and in its temperature profiles, the period of flattening due to boiling is much shorter than is observed for the other samples). However, the 14- and 28-day cured samples show more rapid heat transfer than the 7-day sample, suggesting that convective and conductive heat

transfer effects are beginning to counteract the latent heat effect with the presence of even more water in these samples. Again, a full coupled hygric-thermal model would be required to provide a detailed analysis of all these phenomena, but we believe that the explanations we have developed are capable of describing the experimental observations from an empirical perspective.

3. Pore pressure estimation

The direct measurement of pore pressure during heating of concretes is experimentally an extremely problematic area of research, with published results for Portland cement concretes varying by more than two orders of magnitude depending on experimental setups and sample parameters. There do not exist in the literature (to the best of our knowledge) any previous attempts to estimate pore pressure in geopolymer binders or concretes during heating. Pore pressure is believed to be critical in determining whether a concrete will spall, as the point at which pore pressure exceeds the mechanical properties of the concrete is when spalling may be expected to take place, and much of the research in the past decades aimed at reducing spalling of high-performance concretes has been focused in this area.

We did not measure pore pressures directly. However, it is well known that the temperature at which water boils is a direct function of pressure, and so we have estimated the pore pressures in the geopolymer concrete samples by observing the flattening of the temperature increase profiles (e.g. Figure 1) corresponding to the boiling of water at each different depth in the sample. The results of this analysis are plotted in Figure 4.

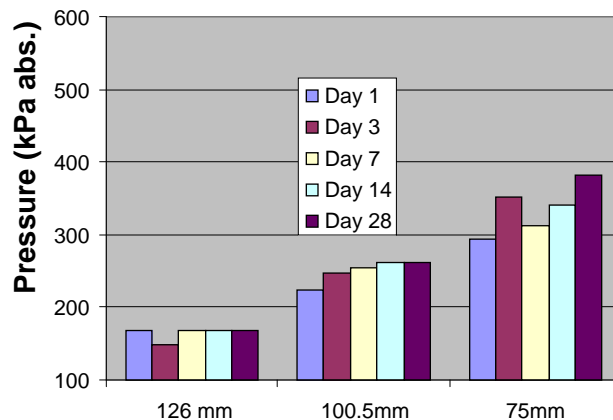


Figure 4. Pore pressures estimated from the boiling points of water at different depths in the interior of the specimens. Data obtained at depths closer to the heated face were very imprecise due to the rapid movement of the boiling front past these thermocouples.

This provides a first estimate of pore pressures at different points within the geopolymer concretes tested. There are, of course, many subtleties related to capillary forces and

effects which are unlikely to be captured by such an analysis, and the flattening is not always distinct, particularly for thermocouples close to the heated face which pass through the boiling regime very rapidly. However, as a pore pressure estimation technique not requiring specialized instrumentation, this method (which, upon a brief literature search, we believe may be novel) is appealing.

4. Spalling

A tendency towards explosive spalling has been noted in many high-performance (and other) concretes, and has been the subject of much investigation internationally over the past 20 years. In fact, one of the original motivations for the early stages of development of geopolymer binders in Europe in the 1970s was in an attempt to develop a fire-resistant, non-spalling material for use in transport tunnel linings following a number of catastrophic tunnel fires in that region. While the early geopolymer materials were not widely used in this application, the issue of spalling (and spalling-resistant high-strength construction materials in general) is certainly an area of interest. The samples tested here are not specifically high-performance mixes (the “E-Crete 40” mix shows a 28-day compressive strength of 40MPa), but higher-strength geopolymer mixes are available, and as a first suite of test samples, we selected a moderate-strength mix to ensure that these samples do not show any undesirable behavior.

Our first fire test trials of geopolymer concretes, using samples which had been cured under sealed conditions but not exposed to ambient conditions for a significant period after unsealing, showed a high degree of spalling as the high water content and very refined pore structure led to the buildup of very high pore pressures. However, the more realistic curing regimes utilized in this work (a period of ambient, unsealed curing replicating the concrete being placed in service for a period of time before being exposed to fire load) did not induce spalling in any of the samples tested.

Figure 5 shows a photograph of the heated face of one of the test samples upon removal from the furnace. The discoloration at the edges of the sample is where the material was in contact with the insulation of the furnace during the test, and the small dark marks on the surface were caused by popping-out of some of the coarse aggregate (gravel) particles as the gravel particles split due to expansion of included fluid (water or air pockets within the rock) upon heating. Following the test, the samples retained their structural integrity, and were able to be lifted and stacked using a forklift without any difficulty or fragility. The heated surfaces of the samples were whitened, slightly dusty and soft, as expected, but the bulk of the sample (which had sustained exposure to temperatures of up to 800°C) did not show structural failure.

We are therefore, in conclusion, very satisfied with the performance of geopolymer concrete under fire testing conditions, as the rate of thermal transport is low, and the degree of structural damage to the materials during a 4-hour fire test is minor.



Figure 5. Photograph of the heated face of a 4'×4'×6" geopolymer concrete sample (cured for 7 days after pouring) following exposure to the Standard Time-Temperature Curve heating profile for 4 hours. Note the absence of spalling; this is typical of all samples tested.